

STABILITY OF HYPOTHETICAL CARBON PHOSPHIDE SOLIDS

ADELE TZU-LIN LIM, JIN-CHENG ZHENG AND YUAN PING FENG

Department of Physics, National University of Singapore, Singapore 119260

Using first-principles calculation, we have investigated the stability of various possible structures for hypothetical carbon phosphide solids with composition C_3P_4 . Unlike C_3N_4 , the calculations predict that pseudocubic- C_3P_4 is energetically favored relative to α - C_3P_4 and β - C_3P_4 . The pseudocubic phase has bulk modulus of 230 GPa, highest among the various structures considered.

1. Introduction

There is considerable interest in the use of C_3N_4 and Si_3N_4 which are well known for their high bulk moduli and wide band gaps as high-performance engineering materials. To date, no research has been done on the properties of C_3P_4 which can be obtained by substituting N for P in C_3N_4 . Based on an empirical model for the bulk moduli of tetrahedrally bonded covalent solids ¹, C_3P_4 is expected to have bulk modulus comparable to that of Si_3N_4 since the sum of ideal tetrahedral covalent bond length between C and P atoms is 1.87 Å which incidently, is the same as that between Si and N atoms ².

Considering the success of first-principles calculation in predicting the electronic and structural properties of C_3N_4 ³, we have performed first-principles total energy calculations based on pseudopotential and plane-wave method on C_3P_4 to investigate the relative stability and structural properties of several possible configurations. To date, we are not aware of any experimental data on crystalline carbon phosphide of any sort. Therefore, we decided to begin with possible configurations of C_3N_4 as suggested in Ref. 4 with N substituted by P.

In this study, we only considered several carbon phosphide structures with stoichiometry C_3P_4 . However, there is no reason *a priori* to believe that only this stoichiometry is possible. Experimental data reveals a wide range of nitrogen concentration even with carbon nitride ^{5–6}. Neither is this stoichiometry confined to the phases considered. The crystal structures considered are α - C_3P_4 , β - C_3P_4 , cubic- C_3P_4 , pseudocubic- C_3P_4 and graphitic- C_3P_4 . We have also calculated the structural properties of β - Si_3N_4 and β - C_3N_4 to lend support to the results obtained for the various phases of β - C_3P_4 .

2. Method

We have performed ground state total-energy calculations using plane-wave pseudopotential method based on density-functional theory (DFT) in the local den-

sity approximation (LDA) for exchange and correlation ⁷. The Vanderbilt ultra-soft pseudopotentials were used ⁸⁻⁹. The wave functions are expanded into plane waves up to an energy cutoff of 310 eV. Special k points generated according to Monkhorst-Pack scheme ¹⁰ were used for integration over the irreducible wedge of the Brillouin zone for the various structures. We used 18 k points for α -C₃P₄, 36 for β -C₃P₄, 32 for cubic-C₃P₄, 32 for pseudocubic-C₃P₄ and 16 for graphitic-C₃P₄. Good convergence is achieved with this cutoff energy and number of k points for the various C₃P₄ structures considered. We also optimized each crystal geometry within preselected space groups.

3. Results and Discussion

Table 1 summarizes the results of our calculation for β -Si₃N₄ and β -C₃N₄. The calculated values for structural parameters and bulk moduli of β -Si₃N₄ and β -C₃N₄ where available are in excellent agreement with experiment.

Table 1. Equilibrium structural parameters and bulk moduli for β -Si₃N₄ and β -C₃N₄.

	β -Si ₃ N ₄		β -C ₃ N ₄	
	Present	Experiment	Present	Experiment
a (Å)	7.531	7.607 ^a	6.380	6.3 ^c
c (Å)	2.875	2.911 ^a	2.396	6.43 ^d
				2.38 ^c
				2.38 ^d
	Si1 (0.174 0.768 0.25)	Si1 (0.174 0.766 0.25) ^a	C1 (0.179 0.773 0.25)	—
	N1 (0.330 0.030 0.25)	N1 (0.321 0.025 0.25) ^a	N1 (0.330 0.033 0.25)	—
	N2 (0.333 0.667 0.25)	N2 (0.333 0.667 0.25) ^a	N2 (0.333 0.667 0.25)	—
B_0 (GPa)	256	259 ^b	443	—

^aBorgen and Seip ¹¹

^bVogelgesang *et al.* ¹²

^cYu *et al.* ¹³

^dZhang *et al.* ⁶

Fig. 1 shows the calculated total energy per C₃P₄ unit as a function of volume for the five structures considered. Unlike C₃N₄, the calculations predict that pseudocubic-C₃P₄ is energetically favored relative to α -C₃P₄ and β -C₃P₄ and has the highest bulk modulus of 230 GPa. Furthermore, β -C₃P₄ is found to be unstable. The calculated total energies are fitted to fourth order polynomial expansion and the bulk modulus for each structure is determined. Table 2 shows the equilibrium structural parameters, bulk moduli and total energies per C₃P₄ unit for each structure. For the calculation of bulk moduli, we have assumed uniform compression and expansion of the lattice. Based on this assumption, we found the bulk modulus of β -Si₃N₄ to be 256 GPa, which is well within the experimental error of Ref. 12. This indicates that our assumption is justified for β -Si₃N₄.

For C₃N₄, the most stable structure among the phases considered in this study is the graphitic-C₃N₄, followed by α -C₃N₄, β -C₃N₄ and cubic-C₃N₄, whereas pseu-

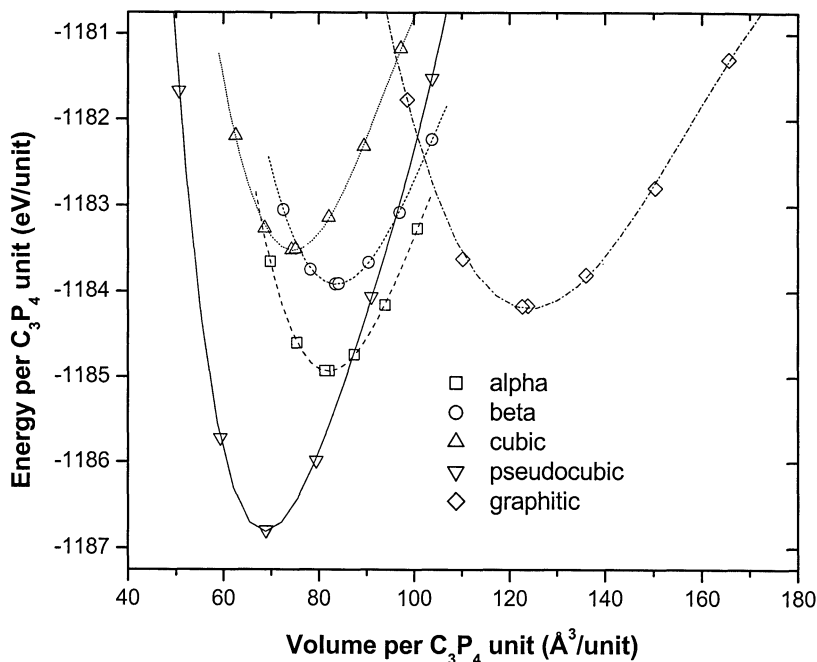


Fig. 1. Total energy as a function of volume for the various structures investigated. The calculated data points are fitted to fourth order polynomial expansion to obtain the bulk modulus for each structure.

Table 2. Equilibrium structural parameters, bulk moduli and total energies calculated for α -C₃P₄, β -C₃P₄, cubic-C₃P₄, pseudocubic-C₃P₄ and graphitic-C₃P₄.

	α -C ₃ P ₄	β -C ₃ P ₄	Cubic-C ₃ P ₄	Pseudocubic-C ₃ P ₄	Graphitic-C ₃ P ₄
Space group	<i>P</i> 3 ₁ <i>c</i> (159)	<i>P</i> 6 ₃ / <i>m</i> (176)	<i>I</i> 4 ₃ <i>d</i> (220)	<i>P</i> 4 ₂ <i>m</i> (111)	<i>P</i> 6 ₃ / <i>m</i> 2 (187)
<i>a</i> (Å)	8.129	8.276	5.780	4.102	5.719
<i>c</i> (Å)	5.742	2.813			8.747
<i>B</i> ₀ (GPa)	174	160	171	230	—
<i>E</i> ₀ (eV/C ₃ P ₄ unit)	-1184.92463	-1183.90798	-1183.51366	-1186.78941	-1184.16285

docubic-C₃N₄ is the least stable⁴. For C₃N₄ in the graphitic, α , β and cubic phase, each C atom is approximately tetrahedrally coordinated by N atoms and each N atom is nearly planarly-threelfold coordinated to C atoms. This suggests sp^3 hybrid on C atom and sp^2 hybrid on N atom. However, pseudocubic-C₃N₄ C–N–C bond angle is close to the sp^3 angle of 109.47°, indicating that the N atoms in the pseudocubic structure form sp^3 rather than sp^2 bonding orbitals¹⁴.

Moving down the periodic table sp^3 hybridization is energetically favorable and therefore the lowest energy configuration for C₃P₄ corresponds to the structure

in which P atoms form sp^3 bonding orbitals, i. e., pseudocubic- C_3P_4 . The C-P-C bond angle of 103.4° in pseudocubic- C_3P_4 is less than the ideal tetrahedral bond angle of 109.47° due to the repulsion from the lone pair electrons directed at an empty C site. The C-P bond length of 1.86 Å in pseudocubic- C_3P_4 is close to the sum of ideal tetrahedral covalent bond length of 1.87 Å². In contrast, P atoms in cubic- C_3P_4 , which is energetically least favorable among the phases considered form sp^2 bonding orbitals. Although the C-P bond length for this phase is also 1.86 Å, the C-P-C bond angle is 114.3° . The stability of graphitic-, α - and particularly β - C_3P_4 , relies on the ability of P atoms to form sp^3 bonding orbitals. Therefore, the displacement of their atomic coordinates from ideal atomic coordinates of C_3N_4 for the respective phases is rather significant, with the β phase displaying the most significant change which is the cause of its structural instability.

4. Conclusion

We have studied the relative stabilities and calculated the structural properties of hypothetical C_3P_4 in the α , β , cubic, pseudocubic and graphitic phases using first-principles calculation. Among the structures considered, the pseudocubic phase is energetically most favored with the highest bulk modulus value of 230 GPa. The calculated lattice constant and bulk modulus for β - Si_3N_4 which are in excellent agreement with experiment lends support to the predicted properties of C_3P_4 .

References

1. M. L. Cohen, *Phys. Rev. B* **32**, 7988 (1985).
2. C. Kittel, *Introduction to Solid State Physics*, 7th ed. (Wiley, New York, 1996).
3. M. L. Cohen, *Science* **261**, 307 (1993).
4. D. M. Teter and R. J. Hemley, *Science* **271**, 53 (1996).
5. A. Bousetta, M. Lu and A. Bensaola, *Appl. Phys. Lett.* **65**, 696 (1994).
6. Z. J. Zhang, S. Fan and C. M. Lieber, *Appl. Phys. Lett.* **66**, 3582 (1995).
7. M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).
8. D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
9. K. Laasonen, R. Car, C. Lee and D. Vanderbilt, *Phys. Rev. B* **43**, 6796 (1991).
10. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
11. O. Borgen and H. M. Seip, *Acta Chem. Scand.* **15**, 1789 (1961). The correct position for N in (c) is $x = 1/3$, $y = 2/3$, $z = 1/4$.
12. R. Vogelgesang, M. Grimsditch and J. S. Wallace, *Appl. Phys. Lett.* **76**, 982 (2000).
13. K. M. Yu, M. L. Cohen, E. E. Haller, W. L. Hansen, A. Y. Liu and I. C. Wu, *Phys. Rev. B* **49**, 5034 (1994).
14. A. Y. Liu and M. Wentzcovitch, *Phys. Rev. B* **50**, 10362 (1994).